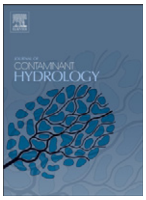
Journal of Contaminant Hydrology 132 (2012) 58–74

Contents lists available at SciVerse ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd



Research article

Time series geophysical monitoring of permanganate injections and in situ chemical oxidation of PCE, OU1 area, Savage Superfund Site, Milford, NH, USA

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ARTICLE INFO

Article history:
Received 27 May 2011
Received in revised form 20 January 2012
Accepted 21 January 2012
Available online 16 February 2012

Keywords:
ISCO
Oxidant
Permanganate
Electromagnetic induction logging
Resistivity
Tetrachloroethylene (PCE)

ABSTRACT

In situ chemical oxidation (ISCO) treatment with sodium permanganate, an electrically conductive oxidant, provides a strong electrical signal for tracking of injectate transport using time series geophysical surveys including direct current (DC) resistivity and electromagnetic (EM) methods. Effective remediation is dependent upon placing the oxidant in close contact with the contaminated aquifer. Therefore, monitoring tools that provide enhanced tracking capability of the injectate offer considerable benefit to guide subsequent ISCO injections. Time-series geophysical surveys were performed at a superfund site in New Hampshire, USA over a one-year period to identify temporal changes in the bulk electrical conductivity of a tetrachloroethylene (PCE; also called tetrachloroethene) contaminated, glacially deposited aquifer due to the injection of sodium permanganate. The ISCO treatment involved a series of pulse injections of sodium permanganate from multiple injection wells within a contained area of the aquifer. After the initial injection, the permanganate was allowed to disperse under ambient groundwater velocities. Time series geophysical surveys identified the downward sinking and pooling of the sodium permanganate atop of the underlying till or bedrock surface caused by density-driven flow, and the limited horizontal spread of the sodium permanganate in the shallow parts of the aquifer during this injection period. When coupled with conventional monitoring, the surveys allowed for an assessment of ISCO treatment effectiveness in targeting the PCE plume and helped target areas for subsequent treatment.

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1. Introduction

In situ chemical oxidation (ISCO) using chemical oxidants, such as permanganate (MnO_4^-), is an effective method of oxidizing anthropogenic chlorinated compounds like tetrachloroethylene (PCE) and similar volatile organic compounds (VOCs). The overall oxidation reaction (Eq. 1) creates several innocuous products such as bicarbonate, chloride, manganese oxides, and proton activity (Cave et al., 2007) and is provided here:

$$4\left(K^+ \text{ or } Na^+\right) MnO^-{}_4 + 3C_2Cl_4 + 4H_2O \rightarrow 6HCO^-{}_3 + 4MnO_{2(S)} + 4\left(K^+ \text{ or } Na^+\right) + 14H^+ + 12Cl^-. \quad (1)$$

This oxidation reaction works only with dissolved contaminants but can accelerate mass removal of contaminants in non-dissolved phases, such as *D*ense *N*on *A*queous *P*hase *L*iquids (DNAPL), by increasing dissolution rates (ITRC, 2005). It also can strip (oxidize) natural carbon from soils and release compounds like PCE that are adhered to the natural carbon (ITRC, 2005).

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0169-7722/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.jconhyd.2012.01.008

The success of delivering oxidants to the targeted contaminated zones is dependent on subsurface conditions and particularly on the spatial distribution of hydraulic conductivity. High hydraulic conductivity is desirable for oxidant distribution (Cave et al., 2007), but other factors are important as well, such as the distribution of the targeted contaminant, oxidant delivery locations, rates, and concentrations, and natural soil oxidant demand (SOD). Importantly, knowledge of the hydraulic conductivity field is needed to optimize the injection.

Petri et al. (2008) found an important relation between remediation effectiveness from ISCO and groundwater velocity, the concentration of injected permanganate and DNAPL architecture. For example, DNAPL mass depletion rates increased with increasing groundwater velocity but under high groundwater velocities, high permanganate concentrations had little additional benefit in the mass removal of contaminants. This illustrates the dependency of ISCO treatment effectiveness to site-specific conditions and the need for enhanced oxidant mapping capabilities to assess treatment efficacy.

Many oxidants possess a strong electrical signal that allows for tracking of injectate transport using time series geophysical surveys (multiple measurements over time) including direct current (DC) resistivity (Zohdy et al., 1974) and electromagnetic (EM) methods (McNeill et al., 1990). Geophysical surveys can enhance the monitoring coverage provided by conventional well sampling and can efficiently cover large areas. Therefore, surveys can provide important information when coupled with conventional monitoring on injectate placement and transport-critical factors in assessing the effectiveness of ISCO treatment.

Time series geophysical surveys with borehole, cross-hole, and surface techniques have been used to map saline tracers and estimate transport properties of aquifers (Day-Lewis et al., 2003; Singha and Gorelick, 2005). More recently, time series surveys have been incorporated into monitoring efforts to track the effectiveness of in-situ remediation of chlorinated anthropogenic compounds (Chambers et al., 2010). Where electrically resistive or conductive injectate are used, delivery of the injectate can be mapped along with the accumulation of chloride from the degradation of chlorinated anthropogenic compounds (Hubbard et al., 2008; Lane et al., 2004, 2006). However, most applications, with a notable exception (Albano et al., 2010), of time series geophysical surveys that track injectate have not used permanganate as a delivery agent despite its strong electrical signal and persistence in the subsurface.

Detailed spatial monitoring during ISCO is necessary to improve our understanding of how the injection of permanganate spreads and if target zones are covered (Cave et al., 2007). The mapping of permanganate can lead to better prediction of contaminant responses to treatment, provide knowledge of the hydraulic conductivity field, and facilitate the design of follow-up treatments. Because each ISCO treatment is expensive, it is advantageous to optimize treatments by understanding the distribution of the injected permanganate, and the necessary amounts of injection to achieve the desired distribution. In almost all cases, the most important aspect of understanding the success of a treatment is the ability to identify areas where permanganate has not spread relative to areas where high PCE concentrations exist.

In this article, we identify the areal and temporal spread of permanganate after injection by use of geophysical time series surveys to identify increases in the bulk electrical conductivity (EC) of a PCE contaminated aquifer, part of the Savage Superfund Site, in the northeastern USA. We also assess the spread of permanganate relative to the hydrostratigraphy of the aquifer, evaluate injectate transport relative to the known PCE distribution, and summarize the overall effectiveness of the injection based on permanganate delivery, transport, and pre and post-ISCO PCE concentrations. Bulk EC increases were compared to specific conductance, permanganate, chloride, and PCE concentrations from conventional monitoring to help differentiate the relative response of bulk EC to the presence of sodium permanganate and chloride from oxidation of PCE. This study provides an example of the use of time series geophysical surveys to facilitate monitoring during ISCO, mapping of injectate movement, and evaluation of treatment effectiveness.

2. Site description

The Savage Municipal Water Supply Superfund Site (Site) contains a large PCE plume (1.3 km^2 area in 1994), within a permeable sand and gravel, glacial aquifer. The plume has been under aggressive remediation since the fall of 1998.

The Site has been divided into two Operable Units: OU1, which has been designated as the primary source contamination area, and OU2, which is the extended groundwater plume. The focus of this paper is on the treatment of PCE within OU1. The OU1 remedial systems consist of a low permeability slurry barrier wall (Fig. 1) that extends from ground surface into the basal till or to the bedrock surface (24 to 31 m (80 to 100 ft) deep) to contain the PCE source material, a pump and treat system with extraction wells inside the barrier wall (containment area) to maintain an inward gradient, and external extraction wells to capture residual contaminants outside the barrier. A vapor extraction system has been intermittently operated within the containment area. Several suspected PCE source areas inside the OU1 containment area have been identified including three former solvent discharge locations: a former drain and pit area (located at a well field, called the INEL well field; Fig. 1), a leachfield, and a surface dump area.

Since 1999 when the extraction wells were turned on, PCE concentrations outside the barrier have decreased from greater than 1000 to less than 10 μg/L. However, PCE concentrations in some areas within the containment area have not decreased and are still above 1000 μg/L as of 2008 (Fig. 1). The estimated amount of PCE mass removed from remedial operations between 1999–2008 equaled 1160 kg (Weston Inc., 2010).

To facilitate remediation inside the containment, a series of ISCO treatments, designated as phases, have been performed including two tests in 2003 (phase 1) and 2004 (phase 2). The difficulty in tracking the spread of permanganate with conventional well sampling methods during phases 1 and 2 prompted the need for advanced monitoring techniques employed in this study during phase 3 (subject of this paper). Phase 3 ISCO treatment occurred in 2008, and focused on deep injection (greater than 19 m deep) of